ADSORPTION PROCESSES IN GAS MASK FILTER CANISTERS: PRACTICAL ASPECTS, NEW MATERIALS AND MODELING

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Abstract. Three topics are addressed related to adsorption processes in gas mask filter canisters. In the first section "practical aspects" two items are addressed: (a) the influence of the flow pattern, i.e. a breathing or pulsating flow versus continuous flow, on the breakthrough behavior; and (b) the risk of desorption: the possibility that adsorbed contaminants are released from the filter. The second section "new materials" deals with the use of carbon monoliths. The third section "modeling" discusses a gas mask model that has been implemented in a software tool that simulates chemical and biological incidents.

Keywords: Adsorption, gas mask, carbon monoliths, modeling, incidents.

1. Practical Aspects

During actual use of a gas mask canister the flow through the activated carbon bed is pulsating, i.e. during inhalation air is drawn through the canister, while during exhalation there is a stand-still of air in the canister. In approval tests for filters mostly a constant flow pattern is applied. The time-averaged gas velocity has to be equal when applying a constant continuous flow or a pulsating flow for a fair comparison of the breakthrough behavior for both cases. Figure 1 shows the respiration pattern with a breathing cycle time of 4 s, that is, during 2 s air is flowing through the canister and the next 2 s the air is still.

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Breakthrough measurements applying continuous and pulsating flows were performed using toluene on shallow activated carbon beds (Norit R1). Toluene is a good representative for the type of vapors for which activated carbon forms a suitable adsorbent. Pulsating flow was studied by using the positive halves of a sinusoidal flow pattern, which closely resembles the actual breathing pattern. Figure 2 shows breakthrough profiles of toluene for constant and pulsating flow, where a bed length was applied of 1.5 cm, a toluene concentration of 7.5 g/m^3, and the time averaged superficial gas velocity was 0.127 m/s. The observed difference between the two breakthrough profiles is very typical: pulsating (breather) flows are found to be less favorable for the breakthrough behavior compared to a constant flow pattern.[1] Furthermore, the difference between the two becomes larger for low concentrations. Since in gas masks the low concentration range is of extreme importance in case of high toxic compounds, this difference becomes even more important. The influence of flow rate on the mass transfer from the bulk gas phase to the surface of the adsorbent particles is ultimately responsible for the difference in breakthrough times.[1] Clearly, pulsating flow is a factor to take into account if one requires a reliable assessment of the performance of an activated carbon canister in practice.

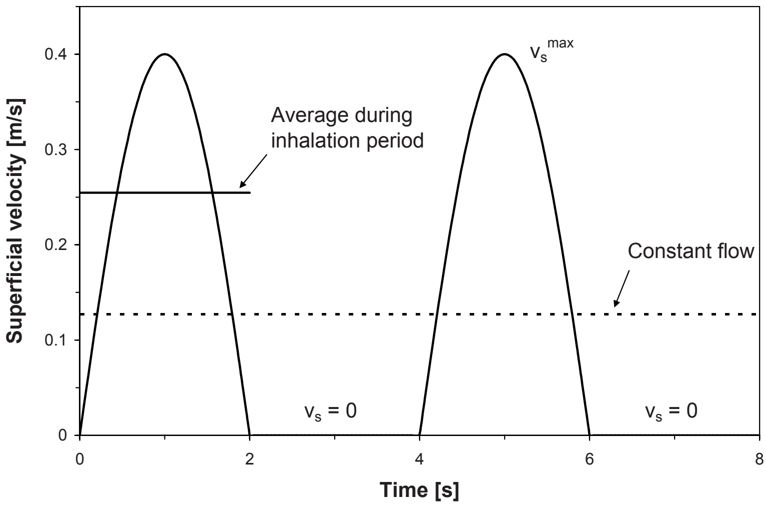

Figure 1. The respiration pattern is represented by a sine wave pattern (solid line), which closely resembles the actual breathing pattern. The dashed line is the corresponding constant flow.

A second practical aspect that is discussed is the risk of desorption.[2] There exists a tendency in industry to equip respiratory protective devices (RPD) with a blower device, which turns them into power assisted devices. The function of the blower is to continuously draw air through the canister

and to blow the air into the protective part around the head of the user. The reason for this approach is obvious: in RPD it is important to have as low a pressure drop as possible. This ensures both a better protection and a higher comfort for the user. This development of equipping RPD with a blower device entails the hazard of desorption. Because air is continuously drawn through the canister, also during exhalation, the possibility increases that adsorbed contaminants are desorbed from the activated carbon. The occurence of desorption was examined under various conditions in order to explore whether or not significant risks exist.

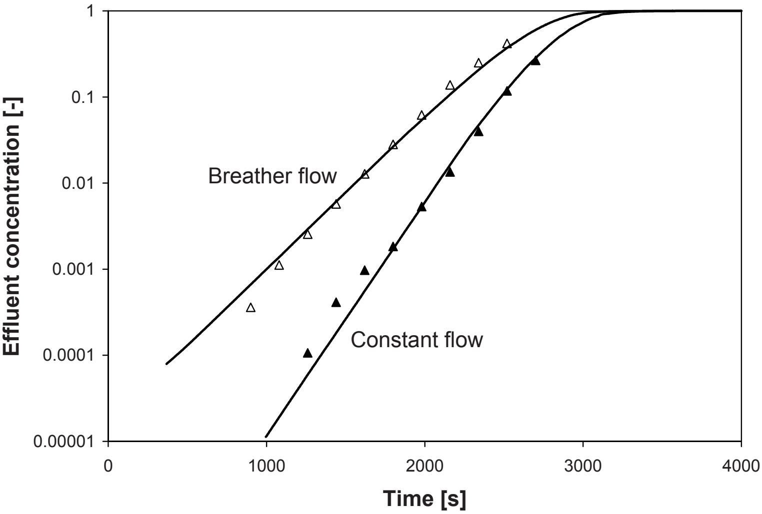

Figure 2. Breakthrough profiles of toluene on Norit R1; comparison between pulsating (breather) and constant flow. The symbols represent the experimental data, the solid lines represent the simulation results.

The existence of a desorption risk was examined by means of a series of sorption experiments in which the same procedure was followed. During a certain period of time a bed of activated carbon was exposed to an air flow containing a contaminant. After this period the supply of the contaminant was stopped while a flow of clean air was continued. The effluent contaminant concentration was monitored during the entire experiment. From the viewpoint of a possible occurrence of a desorption risk it is especially interesting what happens after the supply of contaminant has been stopped. The sorption experiments were carried out with cyclohexane and Norit R1 carbon. The bed height was 2 cm and the total flow rate was 7.5 L/min, which corresponds to a superficial gas velocity of 6.4 cm/s. The entire carbon bed was divided into two separate beds, in series, of 1 cm each. The cyclohexane concentration was monitored gas chromato-graphically after

each bed, providing extra information about the progress of the concentration front.

Figure 3 shows the results of experiments where challenge times for cyclohexane were applied of 10, 20, and 30 min. In all three cases cyclohexane was positively detected after the first part of the bed. The point at which the feed of cyclohexane was stopped, is visible as well: the concentration rises less fast or decreases even at that moment. The system is flushed with clean air that causes the concentration to rise less fast or even to decrease initially. Subsequently, previously adsorbed cyclohexane starts to release: desorption occurs and the concentration shows a further increase. A longer challenge time results in a higher concentration. Although at 20 and 30 min challenge time the concentration rises above the breakthrough criterion of 5 mg/m^3, this is measured halfway through the carbon bed (1 cm). The concentration at the end of the bed is of more importance, as filter canisters are equipped with carbon beds that typically have a bed length of 2 cm. Only in case of a challenge time of 30 min cyclohexane was detected at the end of the bed. This occurred, though, only after more than 200 min; nevertheless, the concentration did rise above the breakthrough criterion of 5 mg/m^3. For 10 and 20 min challenge time no cyclohexane was detected at the end of the bed even after 10–12 h of clean air flow, i.e. the concentration is below the detection limit of 0.01 mg/m^3.

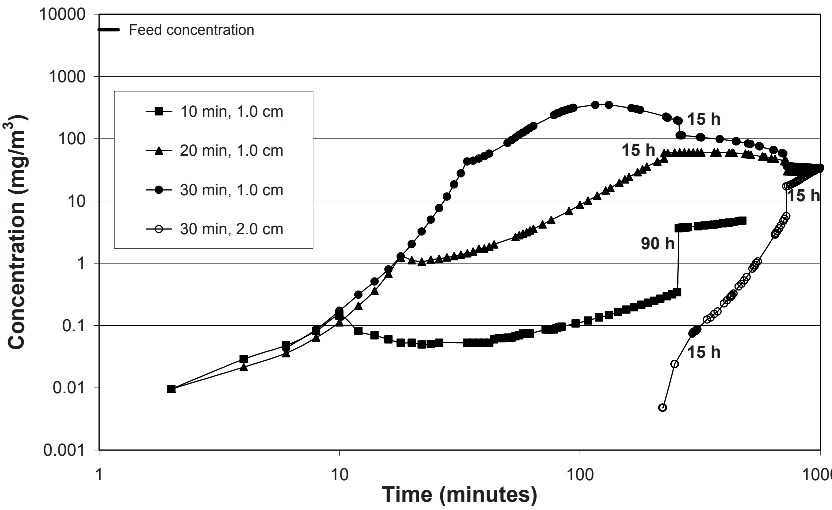

Figure 3. Breakthrough profiles of cyclohexane on Norit R1. The feed concentration was 5.63 g/m^3, supplied during 10, 20, and 30 min; the carbon was dried and the feed humidity was ≤10%. The concentration jumps are a consequence of a period of air standstill.

For a more detailed discussion of the results of this study (including experimental results at different conditions) is referred to the recent publication by Linders et al.[2] It is concluded that physisorbed contaminants

may be released from activated carbon filters in significant concentrations once the influent concentration of the contaminant has been reduced to zero. A redistribution of physisorbed contaminants over the activated carbon bed occurs in a period of rest (e.g. one night or more), which may lead to augmented release of contaminant when the filter is re-used. Under humid conditions the desorption of physisorbed contaminants occurs more rapidly than under dry conditions. Because desorption phenomena pose a risk for the users of RPD, it is advisable to address this somehow in all approval tests for vapor filters.

2. New Materials: Monoliths

The protection against chemical warfare agents is based on sorption on activated carbon, both in gas mask canisters as well as in protective clothing. The carbon applied are granulates (mask) or small spheres (clothing). A new development in adsorption processes is the use of monoliths,[3] either carbon monoliths or carbon-coated ceramic monoliths. Figure 4 shows a carbon monolith. Monoliths consist of many parallel channels separated by thin walls. The main advantages are low-pressure drop and short diffusion distances.

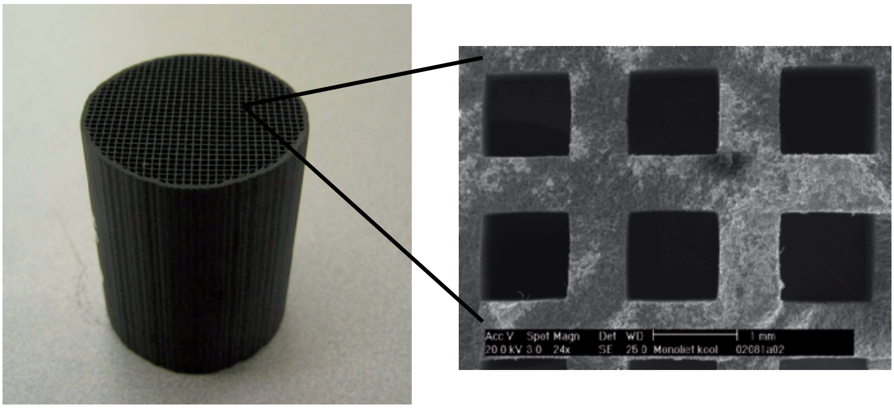

Figure 4. Carbon monolith and detail of the channels on the right.

Carbon and carbon-coated ceramic monoliths have been studied for the dynamic adsorption of low-concentration *n*-butane.[4] Figure 5 shows breakthrough profiles of carbon coated ceramic monoliths and of Norit R1 carbon extrudates. The experiments with Norit carbon were performed with an equivalent amount of carbon as the corresponding monoliths, under similar conditions. Experimental conditions were as follows. The total flow rate was 1.5 L/min, which corresponds to a superficial gas velocity of 0.017 m/s, and the *n*-butane concentration was 7.2 g/m^3 (3,100 ppm). Bed lengths of 5

and 10 cm monolith (made from individual pieces of 5 cm length) were applied at a cell density of 400 cells per square inch (cpsi). Figure 5 clearly shows that breakthrough profiles are much steeper for the coated monoliths compared to carbon extrudates, especially in the low concentration regime. This makes monoliths an attractive option for gas mask canister applications, which is even more so taking into account the low pressure drop (low breathing resistance).

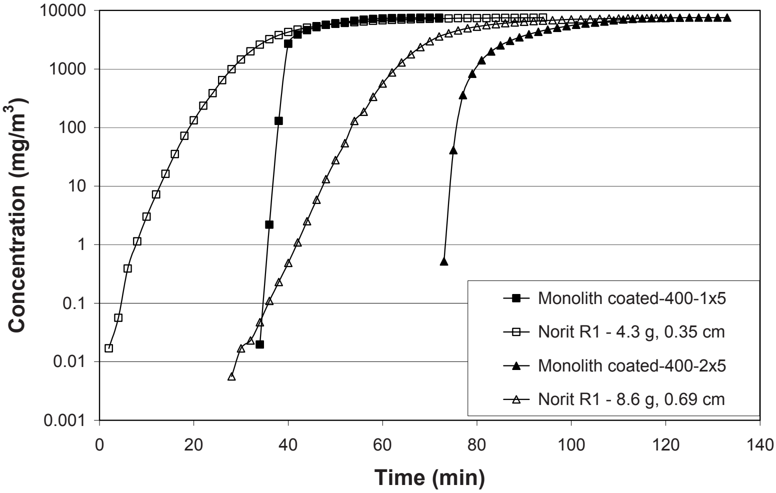

Figure 5. Breakthrough profiles of *n*-butane on carbon coated ceramic monolith and Norit R1 carbon.

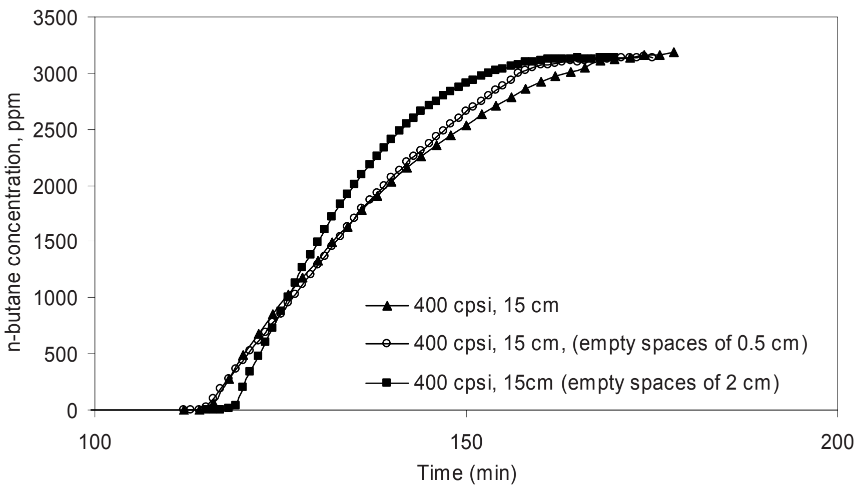

Figure 6. Breakthrough profiles of *n*-butane on carbon coated ceramic monoliths, total length 15 cm; the 5 cm pieces are stacked without empty space and with 0.5 and 2 cm empty space between the pieces.

Another interesting feature is presented in Figure 6. Breakthrough profiles are shown of *n*-butane on carbon coated ceramic monoliths with a total length of 15 cm. The individual 5 cm pieces are stacked without empty space between the pieces and with 0.5 and 2 cm empty space between the pieces. Clearly, empty spaces between the monoliths result in a positive effect on the breakthrough profiles, which become steeper when the empty space is increased. This effect can be related to redistribution of flow between the monolith pieces.

3. Modeling

The gas filter of the presently used gasmasks consists of an activated carbon bed. A two-dimensional mathematical model for physically adsorbed gases was used to describe the dynamic behavior of the activated carbon bed. This model is valid for the adsorption behavior of a vast number of organic contaminants and includes convection, dispersion, external film resistance, macropore diffusion in the sorbent particles, and the Dubinin–Radushkevich model to describe adsorption equilibrium.

A gasmask never fits perfectly, meaning that a certain contribution of leakage is always present. Therefore, apart from the activated carbon filter model a leakage model completes the model of a gasmask. This gas mask model has been implemented in a software tool that simulates chemical and biological incidents.[5] This "Chemical and Biological Incident Simulator" (CABIS) – a chain of linked simulation models (see Figure 7) – simulates the dispersion of chemical and biological warfare agents, detector responses, the effects of protective equipment such as masks and suits, and the human toxicological responses for large numbers of scenarios considered realistic given a certain threat. The ultimate result is an estimation of casualties, varying from mildly affected, severely affected, to the worse category being dead. Next the CABIS model is discussed in somewhat more detail, keeping in mind that the gas mask model is one of its constituent models.

The calculations start by simulating "the agent release and transport" in an incident scenario which results in concentration-time profiles at the locations of detectors and personnel. Figure 8 shows a typical plot of the liquid deposition density on a target area after an attack with a multiple rocket launcher. The detector module generates an alarm-time profile when a chemical or biological agent is detected, an example of which is shown in Figure 9. Based on the concentration-time and alarm-time profiles the skin and respiratory protection models calculate exposure profiles, using given protective equipment characteristics. In this respect Figure 10 shows the influence of wearing respiratory protection on the exposure to sarin.

Finally, the toxic effects module translates the exposure profiles into casualty probabilities for the personnel. Operational behavior, like changes in "Dress State" and typical reaction times are taken into account in the simulations.

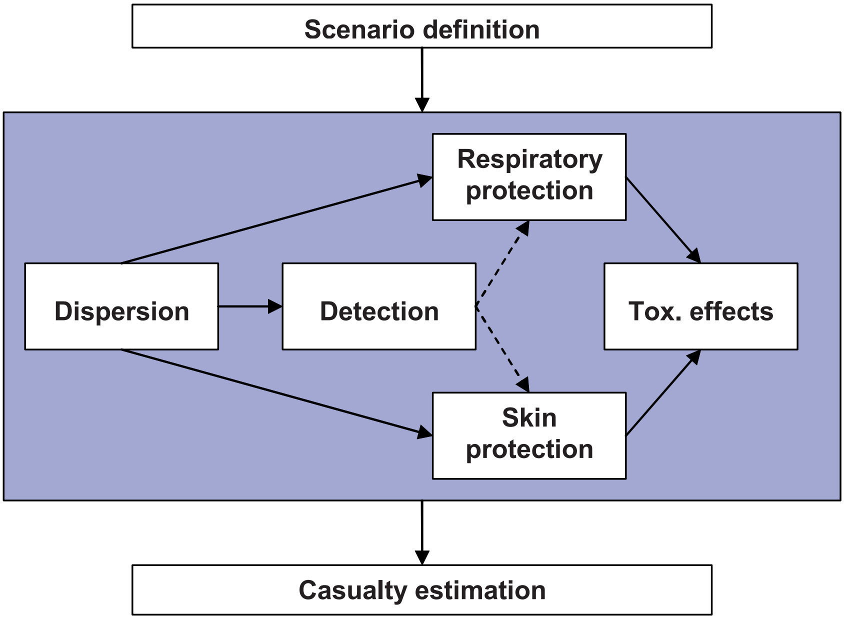

Figure 7. Scheme of the CABIS model chain.

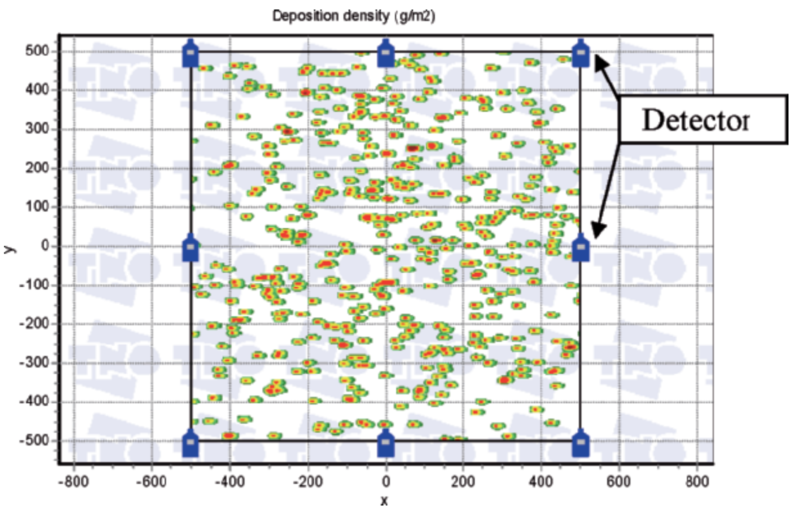

Figure 8. Liquid deposition density of sarin on a target area 500 × 500 m.

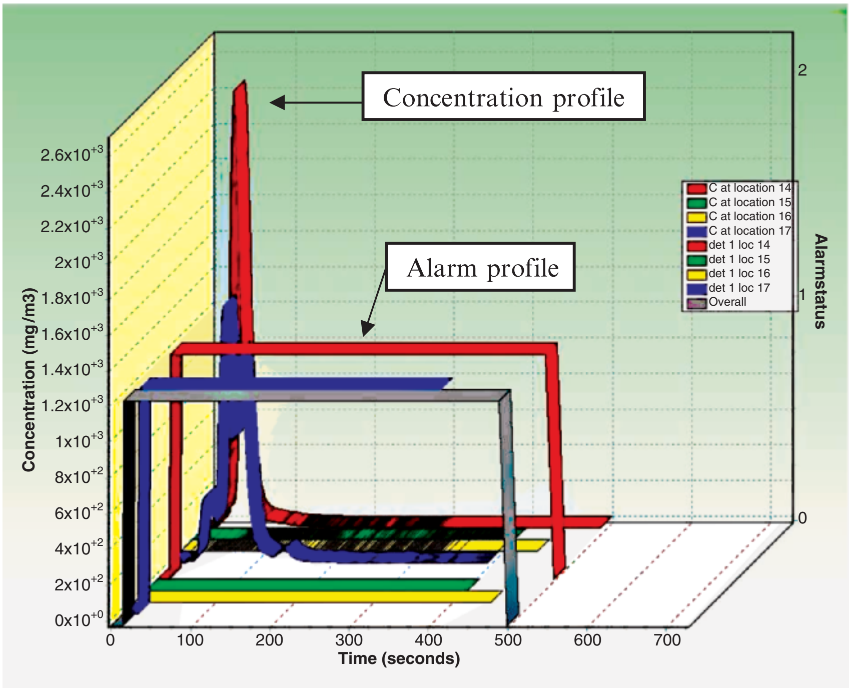

Figure 9. Concentration-time and alarm-time profiles of the individual detectors and the composed overall alarm profile.

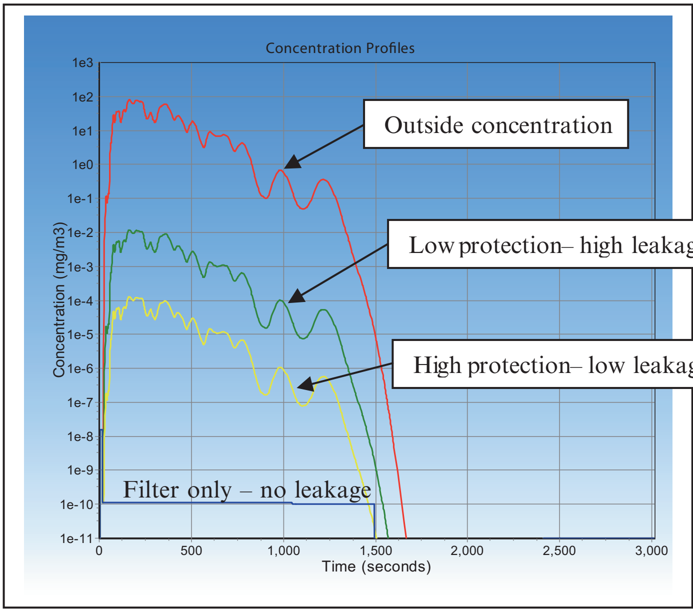

Figure 10. Influence of wearing respiratory protection on the exposure to sarin.

All input parameters, scenario definitions and results are stored in a database for easy access and retrieval. Analysis of individual scenario results and statistical analysis over all scenarios (or any subset) is possible. Typical individual scenario results are the deposition and the dosage on the attacked target, the number of casualties, and the severity of injuries. Typical statistical analysis results are dosage and deposition threat spectra, and casualty spectra. The casualty spectra can be obtained for various health effect levels (eye effect, incapacitation, lethal) and protection levels (no protection, suit only, mask only, mask and suit, collective protection). The CABIS simulation tool thus largely eliminates the subjectivity involved in scenario studies, protective and detector equipment procurement.

Finally, an interesting feature of CABIS is the possibility of distributed computing. This enables many instances of CABIS (running on different computers) to operate simultaneously on scenarios from the same database. A locking mechanism inhibits the write access to one scenario by more than one CABIS instance at a time. In this way a great number of scenarios can be calculated in a short amount of time and multiple users can access scenarios from the same database simultaneously.

Summarizing, the CABIS simulation tool provides useful information on all of the above aspects – dispersion, detection, protection, casualty estimation – as well as on threat analysis, procurement, research policy, and planning operations in order to optimize passive BC defense.

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